Nucleation thermodynamics of oxide during metal oxidation

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The classical theory of nucleation has been extended to describe oxide nucleation during the oxidation of metals. It is found that the localized reaction of oxygen with an underlying metal substrate exerts a very strong influence on the free energy barrier of three-dimensional oxide nucleation, which can be characterized by an interfacial correlation function. Our results show that the nucleation barrier increases with the steepening of the contact angle between the nucleating phase and the substrate. This model is expected to find applicability in other reaction-induced heterogeneous nucleation systems. © *2009 American Institute of Physics*.
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The oxidation of metals is a chemical reaction with significant technological impact in many fields including corrosion, environmental stability, electrochemistry, heterogeneous catalysis, and thin film growth. In the study of metal oxidation, the Wagner theory[1] is frequently employed to predict the parabolic oxide growth for high-temperature oxidation and the Cabrera and Mott theory[2] is commonly cited to explain why metals form a uniform passivation layer at low temperatures. However, these classical oxidation theories suffer serious deficiencies when dealing with initial stages of metal oxidation. For example, it has been experimentally observed that initial oxidation of many metals actually occurs by nucleation, growth and coalescence of epitaxial oxide islands,[3–8] which represent a critical departure from the aforementioned oxidation theories that assume a uniform layer-by-layer growth of an oxide phase starting with a continuous monolayer.

Oxidation involves surface diffusion and formation of oriented oxide nuclei, and this bears a striking resemblance to heteroepitaxy. Among all the existing heteroepitaxial models, the classical nucleation theory provides a compelling framework predicting nucleation rates by establishing the connection between the nucleation barrier and macroscopic measurable properties of crystals such as surface and interface energies and substantial progress has been made toward understanding the kinetics and thermodynamics of heterogeneous nucleation.[9–13] However, unlike most heteroepitaxial systems in which the substrate is nonreactive and just serves as a structure template for heterogeneous nucleation of deposited atoms, the nucleation of oxide islands during metal oxidation is induced by reaction of gaseous oxygen with the metal substrate, i.e., the oxide nucleation requires the consumption of substrate metal atoms as well as deposited oxygen. The role of the metal substrate in the oxide nucleation is therefore twofold: a structure template and a reactant. Figure 1 schematically illustrates the difference for heterogeneous nucleation on nonreactive and reactive substrates. Then, one natural question arises: how does the surface reaction affect the nucleation kinetics? Associated with this question is how the microstructure of the oxide film can be controlled by

controlling the nucleation processes, which would have significant practical implication. For instance, a slow rate of heterogeneous nucleation can lead to the growth of more compact oxide films by reducing the number density of grain boundaries formed from coalescence of oxide islands. Correct answers to these questions are not only very important for proper interpretation of experimental results but also very crucial for manipulating early-stage oxidation processes. The aim of the present work is therefore to study the nucleation thermodynamics of oxide islanding by extending the classical nucleation theory to the field of metal oxidation and examine the effect of the consumption of underlying metal atoms on the oxide nucleation barrier. To the best of our knowledge, such surface reaction effects have not been treated in previous theories of heterogeneous nucleation although reaction-induced heterogeneous nucleation is very common in nature.

A general and simple picture of nucleation of three-dimensional (3D) oxide islands during metal oxidation can be described as follows. Oxygen gas molecules impinge on the metal surface and dissociate. Dissociated O atoms diffuse over the metal surface, where they may react with underlying substrate atoms to form oxide nuclei or be lost to re-evaporation. The kinetics of oxide nucleation depends on the surface diffusivity of oxygen atoms and the nucleation barrier, which is determined by the changes in Gibbs free energy ΔG associated with the formation of an oxide embryo
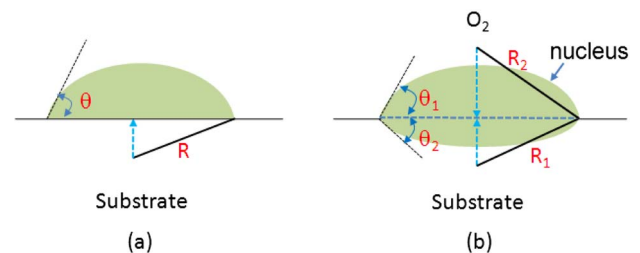

FIG. 1. (Color online) Comparison of heterogeneous 3D nucleation on non-reactive and reactive substrates: (a) a cluster of radius R and contact angle θ forms on a nonreactive surface due to deposition from the vapor phase; (b) the formation of a double cap-shaped oxide island on a metal substrate, where the embedding of the oxide island is caused by the localized reaction, leading to incorporation of underlying substrate atoms into the oxide phase. The upper cap has radius R_1 and contact angle θ_1, and the bottom cap has radius of R_2 and contact angle θ_2.

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$$\Delta G = \Delta G_1 + \Delta G_2, \tag{1}$$

where ΔG_1 corresponds to the volume energy and ΔG_2 represents extra surface and interface energies. The volume energy ΔG_1 can be given by

$$\Delta G_1 = V \times g_v, \tag{2}$$

where V is the nucleus volume, and g_v is the free energy change associated with the oxidation reaction ($M + 1/2 O_2 = MO$) and is equal to $g_v = \Delta G^0 - (1/2)RT \ln P_{O_2}$, where ΔG^0 is the standard free energy change, R the gas constant, and T the oxidation temperature. Because the oxide formation requires reaction between oxygen atoms and their underlying metal atoms, this causes oxide nuclei embedding into the metal substrate. The specific volume of the oxide is rarely the same as that of the metal which is consumed in its formation and the volume ratio between the metal and oxide can be related to the Pilling–Bedworth ratio, $\gamma = V_{ox}/V_m$, where V_m and V_{ox} are the molar volume of the metal and the oxide, respectively.[14] The critical oxide nucleus may be visualized as a double cap-shaped island as shown in Fig. 1(b). The upper cap has radius R_1 and contact angle θ_1 between the oxide-O_2 interface and the metal-O_2 interface. The bottom cap has radius of R_2 and contact angle θ_2 between the metal-oxide interface and the metal-O_2 interface. Because the volume of the embedded part of the oxide is equal to the volume of the consumed metal, we have the following relationship between the total volume of the oxide nucleus and the consumed metal volume

$$V = \tfrac{4}{3}\pi R_1^3 f(\theta_1) + \tfrac{4}{3}\pi R_2^3 f(\theta_2) = \gamma \tfrac{4}{3}\pi R_2^3 f(\theta_2), \tag{3}$$

where the geometric factor $f(\theta)$ depends on the shape of the foreign body on which the heterogeneous nucleation occurs[9,15] and it is equal to $f(\theta) = \frac{(2+\cos\theta)(1-\cos\theta)^2}{4}$ for a plane surface.[16] Note that we assume that the metal atoms incorporated into the oxide island are supplied from the metal substrate underneath the oxide nucleus, i.e., 3D island nucleation.

The extra surface and interface energies ΔG_2 associated with the island formation can be calculated as follows:

$$\Delta G_2 = 2\pi R_1^2(1 - \cos\theta_1) \times \sigma_{NO} + 2\pi R_2^2(1 - \cos\theta_2)$$
$$\times \sigma_{NS} - \pi R_1^2 \sin^2\theta_1 \times \sigma_{SO}, \tag{4}$$

where σ_{NO}, σ_{NS}, and σ_{SO} are the interface energies of the nucleus-O_2, the nucleus-substrate, and the substrate-O_2, respectively. According to the energy equilibrium condition, the contact angles θ_1 and θ_2 are related as follows:

$$\sigma_{NO} \cos\theta_1 + \sigma_{NS} \cos\theta_2 - \sigma_{SO} = 0. \tag{5}$$

To evaluate the critical free energy ΔG^* on the condition of critical nucleus formation, we can substitute the Eqs. (2)–(5) into Eq. (1) and require that $d\Delta G/dR_1 = 0$ and $d\Delta G/dR_2 = 0$. We then have the radius of the critical nucleus

$$R_1^* = -\frac{2}{\gamma g_v}\left[(\gamma - 1)\sigma_{NO} + \frac{\sin\theta_2}{\sin\theta_1} \times \sigma_{NS}\right]$$
$$\text{and}\quad R_2^* = -\frac{2}{\gamma g_v}\left[(\gamma - 1)\frac{\sin\theta_1}{\sin\theta_2}\sigma_{NO} + \sigma_{NS}\right]. \tag{6}$$

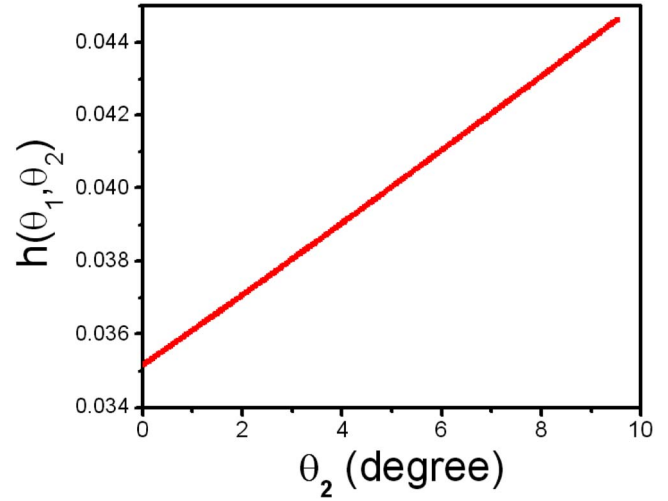Now substituting expression (6) into Eq. (1), the free energy of formation of critical embryo is

FIG. 2. (Color online) Dependence of the factor $h(\theta_1, \theta_2)$ on the contact angle θ_2 of the nucleating phase with the metal substrate.

$$\Delta G^* = \Delta G_{homo}^* h(\theta_1, \theta_2), \tag{7}$$

with

$$\Delta G_{homo}^* = \frac{16\pi}{3 g_v^2}\sigma_{NO}^3, \tag{8}$$

$$h(\theta_1, \theta_2) = \frac{\gamma}{\gamma - 1}\left(\frac{\gamma - 1}{\gamma} + \frac{\sin\theta_2}{\gamma\sin\theta_1} \times \frac{\sigma_{NS}}{\sigma_{NO}}\right)^3 \times f(\theta_1). \tag{9}$$

It should be noted here that the strain energy due to the metal-oxide lattice mismatch is assigned to the metal-oxide interfacial energy σ_{NS} instead of the bulk Gibbs free energy of the oxide island, and this choice has no effect on the outcome of the model calculations. σ_{NS} can thus be expressed by $\sigma_{NS} = \sigma_{chem} + \sigma_{structure}$, where σ_{chem} is the energy term related to the interfacial chemical bonding and $\sigma_{structure}$ is the strain energy due to the lattice mismatch at the metal-oxide interface.[12,17]

We are now in the position to discuss the effect of surface reaction on the nucleation of oxide islands. The expression of ΔG_{homo}^* in Eq. (8) is the barrier for the homogeneous nucleation. $h(\theta_1, \theta_2)$ plays an important role in determining the overall nucleation barrier ΔG^* and one can see from Eq. (7) that the influence of substrate reaction on the nucleation barrier can be fully characterized by the factor $h(\theta_1, \theta_2)$. In Fig. 2, $h(\theta_1, \theta_2)$ is shown as a function of the contact angle θ_2, where the Pilling–Bedworth ratio $\gamma = 1.5$ is used ($\gamma > 1$ for most metal-oxide systems[14]) and values of the surface and interface energy ratios are arbitrarily set as $\sigma_{SO}/\sigma_{NO} = 1/2$ and $\sigma_{NS}/\sigma_{NO} = 1/4$ (note that variations in these ratios do not change the trend of $h(\theta_1, \theta_2)$ as shown in Fig. 2). The plot in Fig. 2 shows a nearly linear dependence of $h(\theta_1, \theta_2)$ on the contact angle θ_2. It can be seen that the factor $h(\theta_1, \theta_2)$ describes quantitatively the decrease of the nucleation barrier from ΔG_{homo}^* to ΔG^* as a function of the inclined angle of the metal-oxide interface. Because the inclined angle θ_2 depends on the localized oxygen-metal interfacial reaction as well as the metal-oxide interface energy as given in Eq. (5), we can define $h(\theta_1, \theta_2)$ as the inter-

facial correlation function that governs the influence of surface reaction on the critical nucleation barrier.

We notice that $\Delta G^*(\theta_2=0) < \Delta G^*(\theta_2>0)$. $\theta_2=0$ corresponds to the situation where oxide embryos do not embed into the substrate. This is possible if both oxygen and metal atoms are mobile and the formation of oxide embryos occurs via collision of oxygen and metal atoms by surface diffusion, i.e., the formation of two-dimensional (2D) nuclei. Although this 2D mechanism (i.e., $\theta_2=0$) offers a reduced nucleation barrier as known from Eq. (7), the probability of oxide nucleation via the collision of metal and oxygen atoms is expected to be small by considering the large difference in their surface mobility. The motion of metal atoms is relatively restricted because atoms have to break their neighboring bonds before they can move freely on the substrate surface. On the other hand, oxygen atoms are highly mobile because their surface diffusion is enhanced by O_2 dissociation and chemisorption, where the energy released from O_2 dissociation and chemisorption processes can be transformed into the kinetic energy of the translational motion of oxygen atoms.[18–21] Therefore, the oxide nucleation is expected to be dominated by the 3D nucleation mechanism where oxygen atoms diffuse over the substrate and react with underlying metal atoms. Under such a 3D nucleation mechanism, the formation of oxide nuclei is accompanied with their embedment into the substrate, and therefore $\theta_2>0$. This 3D nucleation behavior is consistent with our previous experimental observations on the oxidation-reduction cycles of Cu(100) surfaces, which revealed that the reduction in Cu_2O islands on Cu(100) surfaces results in the formation of nanopits at locations which are originally occupied by Cu_2O islands,[22] suggesting that the formation of Cu_2O islands during Cu oxidation is associated with consumption of underlying Cu atoms. Previous *in situ* transmission electron microscopy observations of the early-stage oxidation of Cu(100) and (110) by Yang and co-workers[7,8] also support the 3D oxide nucleation mechanism.

In conclusion, we have extended the classical nucleation theory to the field of metal oxidation, where the heterogeneous nucleation of 3D oxide islands requires the incorporation of underlying metal atoms. It is found that the localized reaction of oxygen with a metal substrate exerts a strong effect on the free energy barrier of 3D nucleation, i.e., the nucleation barrier increases nearly linearly with increasing the contact angle between the oxide phase and the metal substrate. The insights obtained from this study are expected to have broader implications in understanding transient oxidation of metals, where oxide islanding generally occurs but the information on the fundamental processes governing oxide island formation is still very limited. The results may also find applicability in other surface reaction systems such as sulfidation, corrosion, hydriding, and reactive wetting, where the heterogeneous nucleation of new phases also requires the participation of substrate atoms and such a process exhibits great similarity to oxide islanding during the oxidation of metals.

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